UV Absorption Spectrum and Self-Reaction Kinetics of the Cyclohexadienyl Radical, and Stability of a Series of Cyclohexadienyl-Type Radicals

Florence Berho, Marie-Thérèse Rayez, and Robert Lesclaux*

LPCM, UMR 5803 CNRS, Université Bordeaux 1, 33405 Talence Cedex, France

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The UV spectrum, self-reaction kinetics, and stability of the cyclohexadienyl radical (C_6H_7) were investigated by flash photolysis, using a novel method to generate the radical. The absolute UV spectrum was obtained for the first time. It exhibits an intense peak of absorption at 302 nm, similar to that of other cyclohexadienyl-type radicals, with $\sigma_{max} = (2.55 \pm 0.45) \times 10^{-17}$ cm^2 molecule^{-1} at 302 nm (total uncertainty). As the radical was generated in the absence of any other reactive species, the kinetics of the self-reaction could be investigated, leading to $k(C_6H_7+C_6H_7) = (3.1 \pm 1.0) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K. In addition, the equilibrium constant of reaction 1, $H + C_6H_6 \rightleftharpoons C_6H_7$ (1, −1), was measured at 628 and 670 K, and the enthalpy of reaction was derived using the third law method of analysis. The result is $\Delta H°_{298}(H + C_6H_6 \rightarrow C_6H_7) = -(88.4 \pm 12.0)$ kJ mol^{-1} using the calculated value $\Delta S°_{298}(H + C_6H_6 \rightarrow C_6H_7) = -(80.5 \pm 4.0)$ J mol^{-1} K^{-1} (derived from DFT and BAC-MP4 type quantum calculations), corresponding to $\Delta H°_{f,\,298}(C_6H_7) = 212 \pm 12$ kJ mol^{-1}. The experimental work was complemented by theoretical calculations with the objective of establishing a scale of stability of a series of cyclohexadienyl-type radicals XC_6H_6. Calculations were performed for X = F, Cl, Br, H, OH, and CH_3 and the few experimental data available to date were used to validate the results of calculations. The following sequence, from the more to the less stable radical, was established: $FC_6H_6 > HC_6H_6 > HOC_6H_6 > CH_3C_6H_6 > ClC_6H_6 > BrC_6H_6$. The latter three radicals of this series are too unstable for having a chance to be observed in laboratory. The important factors influencing the stability of the XC_6H_6 radical according to the nature of X are discussed.

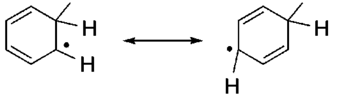
1. Introduction

The cyclohexadienyl radical (C_6H_7) is formed in the gas phase by the equilibrated reaction:

$$H + C_6H_6 \rightleftharpoons C_6H_7 \qquad (1, -1)$$

Very few studies have been reported so far concerning reaction 1 and subsequent reactions of the cyclohexadienyl radical. In contrast, the corresponding reactions of OH radicals with benzene and the reactions of the hydroxycyclohexadienyl radical HOC_6H_6 have been the subject of several kinetic studies, as a result of their atmospheric implications.[1−3]

Cyclohexadienyl-type radicals are resonance-stabilized and radicals resulting from the addition of an atom or radical X on the aromatic ring of benzene can be represented by the two following resonance structures:



According to previous studies, a typical feature of UV absorption spectra of cyclohexadienyl-type radicals consists of an intense peak of absorption around 300 nm, the maximum absorption cross section value being in the range (1−2) × 10^{-17} cm^2 molecule^{-1}.[4] Concerning the cyclohexadienyl radical, the first gas-phase UV spectrum was derived from a pulse radiolysis study of $Ar/H_2/C_6H_6$ mixtures.[5] However, the spectrum could not be put on an absolute scale and the authors pointed out that their results could not be reproduced accurately when changing the experimental conditions. Consequently, they considered that only the general shape of the spectrum was meaningful.

Kinetic studies of the cyclohexadienyl radical reactions are also rather scarce. The self-reaction has never been investigated, and only relative rate constants of association reactions of the cyclohexadienyl radical with other radicals such as methyl, ethyl, isopropyl, and *tert*-butyl were determined.[6−9] In those experiments, the cyclohexadienyl radical was generated by hydrogen abstraction from 1,3-cyclohexadiene using the methyl radical.

Several studies were performed on the temperature dependence of k_1, but extrapolation of the results at 298 K yields fairly scattered values, ranging from 1.65 × 10^{-14} [10] to 6.1 × 10^{-14} cm^3 molecule^{-1} s^{-1}.[5] In contrast, the activation energy seems fairly well-established: 16.6 ± 1.2 kJ mol^{-1}.[4,5,11,12]

There has been only one study of the equilibrium (1, −1) resulting in the experimental determination of the enthalpy of reaction 1. However, this determination was derived from a second law method of analysis and corresponds to an unrealistic value of $\Delta S°_{298}$.[12]

The present work provides the first determination of the absolute UV spectrum of the C_6H_7 radical and the first investigation of its self-reaction kinetics. In addition, a new experimental determination of the enthalpy change of reaction 1 provides reliable data on the stability of this radical. This work was made possible by using a novel method for generating the

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* To whom correspondence should be addressed.

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C_6H_7 radical, taking advantage of the absence of reaction between benzene and the Cl atom.[13]

The experimental study of the stability of the C_6H_7 radical was complemented by a more general theoretical study of the stability of a series of XC_6H_6 radicals. This was performed in order to establish the relative stability according to the nature of X, and to determine if such theoretical calculations could be used to anticipate the stability of cyclohexadienyl-type radicals. Calculations were performed for the C_6H_7 and HOC_6H_6 radicals, to make a comparison between the experimental and theoretical results, and for a series of halogenated cyclohexadienyl radicals ($X = F, Cl, Br$), the stability of the ClC_6H_6 radical having been estimated in a separate publication.[13] The case of $X = CH_3$ was also investigated.

2. Experimental Section

Apparatus. All experiments were performed using the flash photolysis technique, coupled to UV absorption detection to monitor radical concentration in real time. The technique has been described previously [14] and can be briefly summarized as follows.

The reaction cell (a cylinder of 4 cm i.d., 70 cm length) could be heated to 800 K, the temperature being controlled to within ±3 K. Gas mixtures were prepared using calibrated flow controllers and the total flow rate was adjusted so that the reaction cell be replenished between each flash, in order to avoid secondary reactions of products. All experiments were performed at atmospheric pressure 760 ± 10 Torr. Radicals were generated using Cl_2 photodissociation in the presence of H_2 and benzene as described below. A Pyrex tube, surrounding the flash lamp, was used to filter out flash radiation of $\lambda < 290$ nm, thus preventing any direct photodissociation of benzene.

Cyclohexadienyl radical concentrations were monitored by UV absorption spectrometry. The analysis light, provided by a deuterium lamp, passed through the reaction cell and was detected using a monochromator/photomultiplier unit with 2 nm band-pass. Transient signals were recorded using a digital oscilloscope and transferred to a computer for averaging and further data analysis. Kinetic simulations were performed by numerical integration of the system of differential equations representing the complete reaction mechanism, and the calculated total absorption was fitted to the experimental traces using nonlinear least-squares analysis.

Benzene was introduced in the gas mixture by flowing H_2 into liquid benzene, and its concentration was determined from its vapor pressure. Molecular chlorine concentrations were determined from the Cl_2 absorption at 330 nm ($\sigma = 2.56 \times 10^{-19}$ cm^2 molecule^{-1} [15]).

Nitrogen (AGA Gaz Spéciaux, purity >99.995%), hydrogen (Air Gaz, purity >99.995%), nitric oxide (AGA Gaz Spéciaux, 0.96% in N_2, purity >99.995%), and molecular chlorine (Messer, 5% in N_2, purity >99.9%) were used without further purification. Benzene (Aldrich, HPLC grade, purity 99.9+ %) was carefully purified as described previously,[13] in order to avoid reactions of Cl atoms with reactive impurities.

Generation of C_6H_7 Radicals. Cyclohexadienyl radicals were formed by addition of H atoms to the aromatic ring of benzene. The difficulty to produce H atoms "cleanly" by flash photolysis was overcome in this work by taking advantage of the slow reaction of Cl atoms with benzene, as reported in a previous publication.[13] Thus, C_6H_7 radicals were generated by flash photolysis of $Cl_2/H_2/C_6H_6$ mixtures according to the following chemical mechanism:

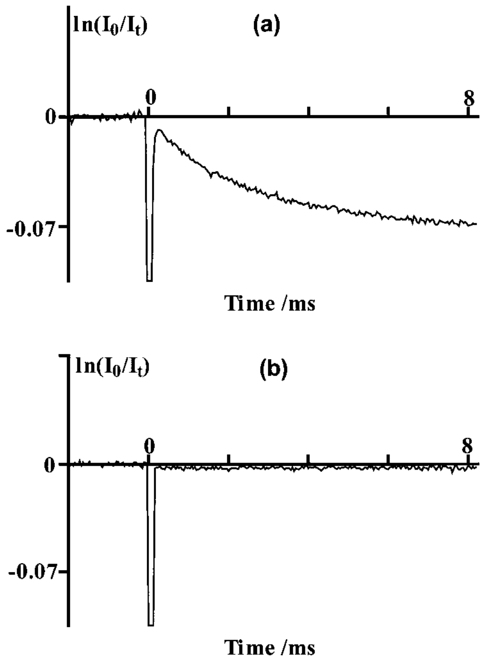


Figure 1. Typical experimental trace recorded at 330 nm following the flash photolysis of a Cl_2/H_2 mixture at 298 K; $[Cl_2] = 4.5 \times 10^{15}$ and $[H_2] \approx 2.5 \times 10^{19}$ (units of molecules cm^{-3}): (a) without benzene; (b) in the presence of benzene ($[C_6H_6] = 3 \times 10^{17}$ molecule cm^{-3}).

$$Cl_2 + h\nu \rightarrow 2Cl$$

$$Cl + H_2 \rightarrow HCl + H \tag{2}$$

$$H + Cl_2 \rightarrow HCl + Cl \tag{3}$$

$$H + C_6H_6 \rightarrow C_6H_7 \tag{1}$$

$$Cl + C_6H_6 \rightarrow \text{products} \tag{4}$$

Reaction 4 is negligible in the presence of excess H_2, as the adduct ClC_6H_6 is highly unstable and the abstraction pathway, leading to HCl and phenyl radicals, is too slow to compete with reaction 2 ($k_4 = 1.3 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} at 298 K[13]). This new method makes it possible to generate the cyclohexadienyl radical in the absence of any other radical species.

One difficulty of this method was the unavoidable chain reaction consuming Cl_2 and propagated by reactions 2 and 3, referred to as the "H_2/Cl_2 chain" in the following. Indeed, Cl_2 absorbs around 300 nm, where the cyclohexadienyl radical was monitored and thus the Cl_2 depletion resulted in distortion of decay traces. The depletion of Cl_2, recorded at 330 nm, is illustrated in Figure 1. Therefore, the H_2/Cl_2 chain had to be accurately characterized to allow precise kinetic studies. This was performed by adjusting the H_2/Cl_2 chain parameters to experimental traces recorded either at 330 nm, or more generally at 350 nm (where only Cl_2 absorbs without any possible interference with any radical or end-product absorption) over long time scales (200 ms), under otherwise identical experimental conditions to those used for kinetic studies.

The reaction of the cyclohexadienyl radical with Cl_2 (reaction 5) can also initiate a chain reaction consuming Cl_2, by Cl atoms regeneration (it will be referred to as the C_6H_7/Cl_2 chain below).

$$C_6H_7 + Cl_2 \rightarrow C_6H_7Cl + Cl \tag{5}$$

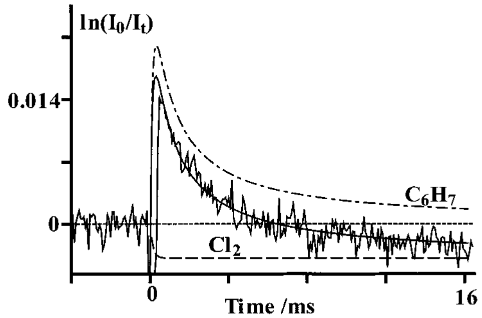


Figure 2. Experimental trace recorded at 302 nm, following the flash photolysis of a $Cl_2/C_6H_6/H_2$ mixture at 298 K; $[Cl_2] = 1.0 \times 10^{16}$; $[H_2] \approx 2.5 \times 10^{19}$; $[C_6H_6] = 3.25 \times 10^{17}$ (units of molecules cm^{-3}).

However, according to experimental traces recorded at room temperature and at 350 nm, this chain reaction was found to be negligible at 298 K and fairly inefficient at higher temperature (see below). It is seen in Figure 1 that no Cl_2 consumption can be related to the C_6H_7 radical disappearance at 298 K, as the total absorption at 330 nm remains constant after the flash, in the presence of benzene.

Another difficulty was due to the relatively slow reaction of Cl atoms with H_2 ($k_2 = 1.65 \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1} [15]) which necessitated the use of large excess of H_2 (nearly 760 Torr). Consequently, H_2 was used as the buffer gas in all experiments. Note that the large excess of H_2 used had the effect of rapidly scavenging Cl atoms, thus preventing their recombination with other radical species.

Experimental conditions had to be properly chosen in order to minimize the influence of the H_2/Cl_2 chain and the resulting distortion of decay traces around 300 nm. This was achieved by using sufficiently high concentrations of benzene, in order to favor reaction 1 at the expense of reaction 3. High concentrations of benzene had also the advantage of minimizing the influence of the recombination reaction ($H + C_6H_7$) by rapidly scavenging H atoms through reaction 1.

Typical concentrations were (units of molecules cm^{-3}): $[C_6H_6] = (3.25-6.5) \times 10^{17}$, $[Cl_2] = (0.5-2) \times 10^{16}$, leading to initial radical concentrations of $(1-6) \times 10^{13}$ molecules cm^{-3}. H_2 was usually used as the buffer gas, except when experiments aimed at verifying that results did not depend on the H_2 concentration, N_2 being then used to balance the total pressure at 760 Torr.

Results and Discussion. *UV Spectrum of the Cyclohexadienyl Radical.* The UV spectrum of the cyclohexadienyl radical was determined in the range 270−315 nm, from the initial absorption of decay traces, resulting from the flash photolysis of $Cl_2/H_2/C_6H_6$ mixtures, at room temperature and atmospheric pressure. A typical signal is presented in Figure 2.

Because of the scattered light from the flash, no information could be obtained for about 200 μs after the flash, and for an accurate determination of the initial absorption, decay traces had to be extrapolated to zero time. Extrapolation was performed by simulation of decay traces obtained on short time scales (20 ms), using the same reaction mechanism and the same procedure as described below for the kinetic study of the self-reaction. An accurate determination of absorption cross sections could not be performed at wavelengths shorter than 270 nm because of the overlap of benzene absorption which resulted in poor signal-to-noise ratios.

Absolute cross sections were determined against those of ClNO. The total initial radical concentration was calibrated by substituting NO for benzene and N_2 for H_2 in the gas mixture, under otherwise identical conditions. NO concentrations were around 4×10^{16} molecules cm^{-3}, so that less than 2% of Cl atoms were lost by reaction with ClNO. The constant absorption of ClNO was observed at 220 nm, where the absorption cross section is known to be $\sigma = 8.96 \times 10^{-18}$ cm^2 $molecule^{-1}$.[15] Care was taken to keep the same Cl_2 concentration in the gas mixture.

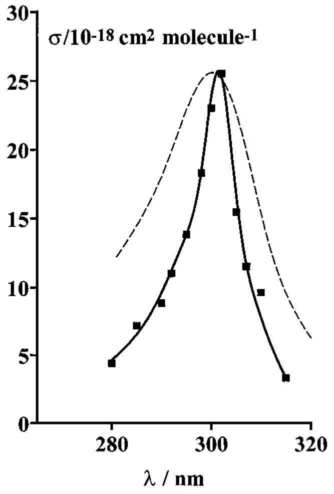


Figure 3. UV spectrum of the cyclohexadienyl radical C_6H_7. The dashed line represents the spectrum reported in ref 5 (under 50 atm of argon), normalized to our spectrum. See also Note Added in Proof.

TABLE 1: UV Absorption Cross Sections of the Cyclohexadienyl Radical

λ/nm	$\sigma(C_6H_7)$ /10^{-18} cm^2 $molecule^{-1}$	λ/nm	$\sigma(C_6H_7)$ /10^{-18} cm^2 $molecule^{-1}$
280	4.38	300	23.0
285	7.15	302	25.5
290	8.84	305	15.4
292	11.8	307	11.5
295	13.8	310	9.6
298	18.3	315	3.3

The resulting values of the absorption cross sections of the cyclohexadienyl radical are reported in Table 1. The UV spectrum of the C_6H_7 radical is represented in Figure 3 and it was found to be in fairly good agreement with the relative spectrum previously reported by Sauer et Ward.[5] Both spectra exhibit an intense peak of absorption around 300 nm, which seems to be a typical feature of cyclohexadienyl-type radicals.[4] In this work, the maximum of absorption was located at 302 nm, and the corresponding absorption cross section value was determined to be $(2.55 \pm 0.10) \times 10^{-17}$ cm^2 $molecule^{-1}$ (1σ).

Only one relative UV spectrum of the cyclohexadienyl radical, determined in the gas phase by pulse radiolysis, had been reported in the literature,[5] and thus no comparison of absolute cross sections can be made. The position of the maximum and the shape of our spectrum are in fairly good agreement with the previous determination, but the peak of absorption determined in the present work is much narrower than that reported by Sauer and Ward.[5] The most likely reason for the difference is the much higher pressure at which the spectrum of Sauer and Ward was recorded, 50 atm argon, instead of 1 atm H_2 in the present experiments, which may have resulted in significant broadening of the peak. The narrow shape of our spectrum points out that our method must be a clean source of the C_6H_7 radical. A good reproducibility was observed for the absorption cross-section values when changing the reactant concentrations in the ranges given above. This shows that the procedure used to account for the Cl_2 consumption by the H_2/Cl_2 chain was appropriate.

TABLE 2: Reaction Mechanism Used in Simulations

reaction	no.	k_{298}/cm^3 molecule^{-1} s^{-1}	$k(T)$/cm^3 molecule^{-1} s^{-1}	ref
$Cl + H_2 \rightarrow HCl + H$	2	1.65×10^{-14}	$3.7 \times 10^{-11} \times \exp(-2300/T)$	16
$H + C_6H_6 \rightarrow C_6H_7$	1	2.0×10^{-14}	$1.65 \times 10^{-11} \times \exp(-2000/T)$	*a*
$H + Cl_2 \rightarrow HCl + Cl$	3	2.0×10^{-11}	$8 \times 10^{-11} \times \exp(-416/T)^b$	this work
$Cl + C_6H_6 \rightarrow$ products	4	1.3×10^{-16}		13
$C_6H_7 + Cl_2 \rightarrow C_6H_7Cl + Cl$	5	$< 10 \times 10^{-14}$	6.2×10^{-13} at 628 K 1.3×10^{-12} at 670 K	see text
$H + C_6H_7 \rightarrow C_6H_8$	6	2×10^{-10}	constant	estimate
$C_6H_7 + C_6H_7 \rightarrow$ products	7	3.1×10^{-11}	$3 \times 10^{-11} \times (T/298)^{-1}$ (estimate)	this work
$Cl + C_6H_7 \rightarrow ClC_6H_7$	8	1×10^{-10}	constant	estimate
$C_6H_7 \rightarrow H + C_6H_6$	−1	negligible	$k = (6500 \pm 2000)$ s^{-1} at 628 K $k = (1.4 \pm 0.4) \times 10^4$ s^{-1} at 670 K at 760 Torr of H_2	this work

[a] Average of the values listed in NIST kinetic database. [b] Adjusted to fit the Cl_2 consumption in the present experiments between room temperature and 600 K; this expression is in good agreement with that recommended by Baulch et al.[20]

TABLE 3: Rate Constant of the Cyclohexadienyl Radical Recombination Reaction (P = 760 Torr, M = H_2) at Room Temperature

[C_6H_6]/molecule cm^{-3}	[Cl_2]/molecules cm^{-3}	[radicals] /molecules cm^{-3}	λ/nm	$k(C_6H_7+C_6H_7)$/cm^3 molecule^{-1} s^{-1}
3.25×10^{17}	2×10^{16}	4.7×10^{13}	280	3.08×10^{-11}
3.25×10^{17}	2×10^{16}	4.7×10^{13}	285	2.13×10^{-11}
3.25×10^{17}	2×10^{16}	4.7×10^{13}	290	2.41×10^{-11}
3.25×10^{17}	2×10^{16}	4.7×10^{13}	292	3.45×10^{-11}
3.25×10^{17}	2×10^{16}	4.7×10^{13}	295	3.17×10^{-11}
3.25×10^{17}	2×10^{16}	4.7×10^{13}	298	3.36×10^{-11}
3.25×10^{17}	2×10^{16}	4.7×10^{13}	300	3.64×10^{-11}
3.25×10^{17}	2×10^{16}	4.7×10^{13}	302	3.00×10^{-11}
3.25×10^{17}	2×10^{16}	4.7×10^{13}	305	2.90×10^{-11}
3.25×10^{17}	2×10^{16}	4.7×10^{13}	310	3.92×10^{-11}
3.25×10^{17}	2×10^{16}	4.7×10^{13}	315	2.97×10^{-11}
3.25×10^{17}	1×10^{16}	2.5×10^{13}	302	3.80×10^{-11}
3.25×10^{17}	5×10^{15}	2.8×10^{13}	302	2.19×10^{-11}
3.25×10^{17}	6×10^{15}	1.3×10^{13}	302	3.38×10^{-11}
6.5×10^{17}	1×10^{16}	2.5×10^{13}	302	3.27×10^{-11}
		average		$(3.10 \pm 1.0) \times 10^{-11}$

Uncertainties arose from the errors on the total initial radical concentration (10%, resulting from 10% uncertainty on the ClNO absorption cross section), from statistical error (6%) and to a negligible extent from the uncertainty of the rate constants of reactions 1 and 6 (20% uncertainty on k_1 and k_6 resulting in 5% and 4% uncertainty on $\sigma(C_6H_7)$, respectively). The influence of uncertainties on k_3 and k_8 had a negligible influence on k_7. An analysis of propagation of errors[16,17] resulted in 18% for the global uncertainty on the absorption cross sections of the cyclohexadienyl radical.

Kinetics of the Cyclohexadienyl Radical Self-Reaction. The rate constant corresponding to the cyclohexadienyl radical self-reaction

$$C_6H_7 + C_6H_7 \rightarrow \text{products} \qquad (7)$$

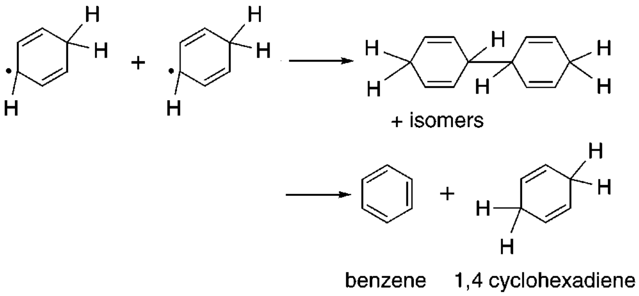
has never been measured before. In this work, decay traces were recorded over 20 ms, by flashing Cl_2 in the presence of benzene, at 760 Torr, hydrogen being used as the buffer gas in all experiments. The kinetics were close to second order but at longer reaction times, the total absorption was observed to become negative, due to the Cl_2 consumption by the chain reactions. Thus, concentrations of reactants had to be properly chosen, as detailed above, for accurate analyses of decay traces. A typical signal is depicted in Figure 2.

Decay traces were simulated using the reaction mechanism presented in Table 2. Based on the consumption of Cl_2 observed at 350 nm, over long time scales (200 ms), the parameters corresponding to the H_2/Cl_2 chain (essentially k_3) were adjusted in the presence of benzene, under exactly the same experimental conditions as those used for the determination of k_7. In addition, it was verified that the value derived for k_7 was independent of (i) the initial radical concentration, (ii) the concentrations of Cl_2 and C_6H_6 when varied over the ranges quoted above, and (iii) the wavelength. The values derived from simulations under various experimental conditions and at several wavelengths are reported in Table 3, the final result being

$$k_7 = (3.1 \pm 1.0) \times 10^{-11}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1} \text{ at 298 K}$$

The quoted uncertainty represents the statistical dispersion of measurements at various wavelengths. Major sources of systematic uncertainties are the initial radical concentration (≈10%), the uncertainty on the absorption cross section (18% global uncertainty as described above), and the rate constant of reaction 6 (<50%). Minor sources of uncertainty are the rate constants of reactions 1 and 3 (a 20% uncertainty on k_1 and k_3 both resulting in an about 10% uncertainty on k_7). It was found that the rate constants of reactions 2 and 8 had no significant influence on k_7. From a propagation of errors analysis,[16,17] the systematic error was estimated at 29%, and thus the global uncertainty on k_7 at ≈42%.

The reaction products were not investigated in this work, but according to previous work performed in the gas phase,[5,9] both the association and disproportionation reaction pathways have been observed to occur. The former yields the different possible isomers of the dimer, corresponding to the two resonance structures of the C_6H_7 radical (see introduction), and the latter yields essentially 1,4-cyclohexadiene (and small amounts of 1,3-cyclohexadiene) along with benzene. The 1,4-cyclohexadiene is formed in greater amounts than the 1,3-cyclohexadiene, in agreement with the principle of least motion, previously described.[18] Sauer et Ward [5] estimated the association rate to be about twice that of disproportionation at room temperature.



The unique measurement of the C_6H_7 recombination rate constant has been performed in the present work. The temperature dependence was not investigated because it is expected to be small and measurements could possibly be slightly influenced by the enhancement of the H_2/Cl_2 and the C_6H_7/Cl_2 chain rates when increasing the temperature. Nevertheless, according to the experiments performed at 628 and 670 K for the equilibrium study (see below), a variation close to T^{-1} can be estimated for k_7. No significant pressure effect is expected for the association reaction of two species of the size of the C_6H_7 radical and thus, it was not investigated.

Stability of the C_6H_7 Radical.

$$H + C_6H_6 \rightleftharpoons C_6H_7 \qquad (1, -1)$$

As the cyclohexadienyl radical can potentially be formed in combustion systems involving aromatic compounds, it is of interest to know in which conditions of temperature it can exist. The thermochemical parameters of reaction 1 have been determined in this work by investigating the equilibrium (1, −1).

The equilibrium has only been investigated once by Nicovich and Ravishankara,[12] in the range 515−570 K, H atoms being generated by directly photolyzing benzene. The value of ΔH°_{298} was then derived from their experimental results, using the second law method of analysis. However, it should be noted that their determination, $\Delta H^\circ_{298} = -110$ kJ mol^{-1}, must bear a fairly large error since the corresponding value of ΔS°_{298} is unrealistic, as it cannot be accounted for by the structure of the C_6H_7 radical. From those data, Tsang performed a third law analysis,[19] using only the value of the equilibrium constant measured at 550 K, the mean temperature of the range investigated. This yielded $\Delta H^\circ_{298} = -92$ kJ mol^{-1}. The present work aimed at providing a new experimental determination of ΔH°_{298}.

Results. The equilibrium was investigated at temperatures up to 670 K. At each temperature, traces were recorded for about 10 values of the benzene concentration, which was varied by a factor of 8−15. At the highest temperature, it was verified that the UV spectrum corresponding to the observed transient signals was the same as that determined at room temperature for the C_6H_7 radical.

Typical concentrations of reactants were (units of molecules cm^{-3}): $[H_2] = (1.1-1.3) \times 10^{19}$, $[C_6H_6] = (0.2-8.0) \times 10^{17}$, $[Cl_2] = (6-7) \times 10^{15}$, leading to initial radical concentrations of $\approx 1 \times 10^{13}$ molecules cm^{-3}. The initial radical concentration was determined by simulation of the initial absorption due to the C_6H_7 radical just after the flash, in the presence of large excess of benzene. The chemical system used in simulations was the same as before, and the relevant rate constants are listed in Table 2.

The system was found more difficult to analyze than at room temperature, because of the enhancement of the Cl_2 consumption. This mainly resulted from the higher H atoms concentration due to the equilibrium (propagating the H_2/Cl_2 chain) and, to a lesser extent, from the enhancement of the H_2/Cl_2 chain rate resulting from the positive temperature dependence of k_3. The value of k_3, derived from the rate expression recommended by Baulch et al.,[20] was found slightly too high to properly simulate the Cl_2 consumption rate. This was not surprising as the temperature-dependent rate expression of k_3 bears a fairly large uncertainty. k_3 was then adjusted, under our experimental conditions, at low benzene concentration and for temperatures where the occurrence of the equilibrium was negligible ($T <$ 600 K), to fit the observed Cl_2 consumption rate. The resulting rate expression is given in Table 2. It should be noted that it remains in agreement with the expression recommended by Baulch,[20] within uncertainties. The rate expression was then extrapolated to the temperature range of the equilibrium study (up to 670 K).

Reaction 5 ($C_6H_7 + Cl_2$) also contributes slightly to the consumption of Cl_2, but no data are available concerning the temperature dependence of k_5. The contribution of this reaction was difficult to separate from that of the H_2/Cl_2 chain, but it could be roughly estimated from the shape of the decay curve at the highest benzene concentrations. It should be noted that the value of k_5 had little influence on the determination of the equilibrium constant, as it influences essentially the shape of the simulated decay curve at longer reaction times, whereas the equilibrium constant value is essentially determined by the beginning of the decay.

From the simulation of experimental traces, the rate constant k_7 for C_6H_7 radical recombination was estimated at $\approx 1 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, which corresponds roughly to a T^{-1} temperature dependence according to the determination at 298 K. This temperature dependence is reasonable but it is no more than a rough estimate as this rate constant was not a sensitive parameter in simulations.

No evidence of the occurrence of an equilibrium could be detected below 600 K. Only at 628 and 670 K decay traces showed unambiguously the presence of an equilibrium, because of a significant enhancement of the Cl_2 consumption due to the persistence of H atoms at equilibrium. This enhancement was indeed much larger than that expected from the normal increase of k_3 and k_5 with temperature. Decay traces could only be properly simulated by introducing the reverse reaction (−1), as illustrated in Figure 4.

The equilibrium constant was determined by adjusting k_{-1} in simulations, for various benzene concentrations. In reality, the only important parameter in simulations was the ratio k_1/k_{-1} and not the individual values of k_1 and k_{-1}. The results are given in Table 4. The global uncertainties on the equilibrium constant values were estimated at 40−50%, using the method of propagation of errors.[16,17] As stressed above, the principal sources of errors were the parameters describing the H_2/Cl_2 chain, particularly the value of k_3. The other important parameters were the concentration of benzene, $\sigma(C_6H_7)$, and $\sigma(Cl_2)$. The errors on the values of k_5 were not significant compared to others.

No more than two experimental values of the equilibrium constant could be obtained as, under our experimental conditions, the equilibrium could not be seen below 600 K, and complications arose at temperatures higher than 670 K, probably as a result of Cl_2 thermolysis. With no more than two experimental points on the Van't Hoff plot, only the third law

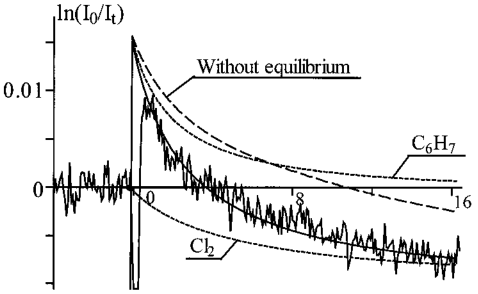


Figure 4. Experimental trace recorded at 302 nm following the flash photolysis of a $Cl_2/C_6H_6/H_2$ mixture at 670 K; $[Cl_2] = 5 \times 10^{15}$; $[C_6H_6] = 2.5 \times 10^{17}$; $[H_2] = 1.6 \times 10^{19}$ (units of molecules cm^{-3}). The solid line represents the fit of experimental data when considering the presence of the equilibrium and the dashed line represents the simulation obtained when ignoring the presence of the equilibrium ($k_{-1} = 0$). Dotted lines represent the contribution of the absorption of Cl_2 and C_6H_7 radical to total absorption.

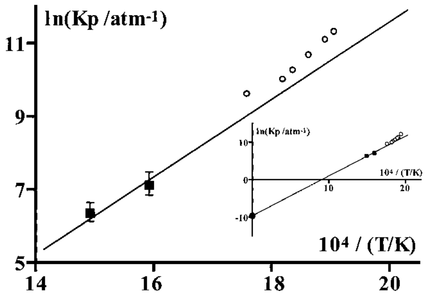


Figure 5. Experimental values of $\ln(K_p)$ against $1/T$: (■) this work; (○) experimental results of Nicovich and Ravishankara;[12] Insert: (●) calculated value of the intercept $\Delta S°_{298}/R$; The solid line is the Van't Hoff line resulting from a third law analysis of our experimental data (see text).

method could allow us to derive reliable thermochemical parameters for reaction 1. This method consists in calculating the value of $\Delta S°_{298}$ using statistical thermodynamics and deriving $\Delta H°_{298}$ from the experimental values of the equilibrium constant, from the slope of the Van't Hoff line, forced to pass through the calculated value of $\Delta S°_{298}/R$.

The entropy variation of reaction 1 was calculated using both DFT and ab initio (BAC-MP4 type) calculations, those methods being described below (see section 3). The DFT and BAC-MP4 methods yielded −82.5 and −78.3 J K^{-1} mol^{-1}, respectively, for $\Delta S°_{298}$. As both methods yielded a similar value for $\Delta S°_{298}$, the average was chosen to apply the third law method to our experimental data, i.e.

$$\Delta S°_{298} = -(80.5 \pm 4.0)\ \mathrm{J\ mol^{-1}\ K^{-1}}$$

The quoted uncertainty was calculated from uncertainties estimated for the lowest vibrational frequencies. The Van't Hoff plot, obtained using the experimental data of the equilibrium constant and the calculated value of $\Delta S°_{298}$, is shown in Figure 5. The resulting enthalpy of reaction 1 is

$$\Delta H°_{298} = -(88.4 \pm 12.0)\ \mathrm{kJ\ mol^{-1}}$$

The uncertainty quoted here combines that estimated on the calculated value of $\Delta S°_{298}$ and the experimental uncertainty on the equilibrium constant, mainly resulting from the absorption cross section of the C_6H_7 radical and from the characterization of the H_2/Cl_2 chain. The variation of reaction enthalpy between 298 K and the temperature range of measurements was calculated to be negligible compared to uncertainties.

The corresponding expression of the equilibrium constant is

$$\ln(Kc/\mathrm{cm^3\ molecule^{-1}}) = -(52.8 \pm 1.0) + [(9.03 \pm 1.20) \times 10^3\ \mathrm{K}/T]$$

The enthalpy of formation of the C_6H_7 radical at 298 K can be derived from the above value of $\Delta H°_{298}$ and the known values of the enthalpy of formation of H atoms and of benzene, 218 and 82.8 kJ mol^{-1}, respectively:[21,22]

$$\Delta H°_{f,298}(C_6H_7) = 212 \pm 12\ \mathrm{kJ\ mol^{-1}}$$

It happens that this value is in very good agreement with that proposed by Tsang,[19] 208.9 kJ mol^{-1}, derived from a third law method of analysis of the previous determination of the equilibrium constant at 550 K (average of the temperature range) by Nicovich and Ravishankara.[12] This is quite satisfying, given the rather large uncertainty on the equilibrium constant determinations, both in the present and previous works.[12] Note, in addition, that this value is consistent with that derived from quantum calculations, as shown below.

Discussion. The equilibrium constant could only be measured in a narrow temperature range. However, we consider that the experimental results are significant as experiments performed using various benzene concentrations yielded similar values for the equilibrium constant at a given temperature. In addition, our experimental measurements of the equilibrium constant are in fair agreement with those obtained previously at lower temperatures by Nicovich and Ravishankara.[12] It should be noted that, as shown in Figure 5, the agreement is better in the upper end of the temperature range investigated by these authors, whereas experimental points obtained at lower temperatures deviate from the regression line. In addition, extrapolating their results obtained in the temperature range 515−570 K to the temperatures of the present study would yield equilibrium constant values about twice lower than our values. Considering the difficulties of measurements and the very different chemical systems used, the difference is reasonable. Indeed, our final result for $\Delta H°_{298}$ is in very good agreement with the value derived by Tsang.[19] In addition, it is shown below that the $\Delta H°_{298}$ value is consistent with that derived from quantum calculations.

It should be noted that the *A* factor for the C_6H_7 radical dissociation was estimated at $\approx 5 \times 10^{12}$ s^{-1} from our experimental results on k_{-1}, using an average activation barrier of 16.5 kJ mol^{-1}. This is also in reasonable agreement with the value derived by Tsang[19] ($A \approx 1 \times 10^{13}$ s^{-1}). In addition, this result is also consistent with those found for reactions of H-atom elimination from other radicals, the *A* factor being $\approx 5 \times 10^{12}$ s^{-1} in the case of the isopropyl radical and in the range 4×10^{12} to 8×10^{13} s^{-1} for butyl-type radicals.[19] However, it should be noted that our determination of k_{-1} is not an absolute value, as individual values for k_1 and k_{-1} were not necessary to determine the equilibrium constant, only the ratio k_1/k_{-1} being used in simulations. As the values of k_1 reported in the literature [5,10−12] differ by at least a factor of 2 in the temperature range of interest, this uncertainty adds to that on our determination of k_{-1}.

3. Stability of a Series of Cyclohexadienyl-type Radicals: A Theoretical Study

The experimental work presented in section 2 was complemented by quantum calculations of thermochemical parameters

TABLE 4: Measured Values of the Equilibrium Constant at 628 and 670 K for Reaction 1

T/K	[C_6H_6] /molecules cm^{-3}	no. of expt	$k_1{}^a$/cm^3 molecule^{-1} s^{-1}	k_{-1}/s^{-1}	K_c/cm^3 molecule^{-1}	K_p/atm^{-1}
628	$(2.5-37.7) \times 10^{16}$	10	6.8×10^{-13}	$(6.5 \pm 2.0) \times 10^{3}$	$(1.05^{+0.5}_{-0.25}) \times 10^{-16}$	$(1.22^{+0.55}_{-0.29}) \times 10^{3}$
670	$(9.6-77.0) \times 10^{16}$	12	8.4×10^{-13}	$(1.6 \pm 0.4) \times 10^{4}$	$(5.25^{+1.8}_{-1.0}) \times 10^{-17}$	$(5.75^{+1.91}_{-1.15}) \times 10^{2}$

[a] Calculated from the expression given in Table 2.

TABLE 5: Calculated Thermochemical Parameters for Reactions X + $C_6H_6 \rightarrow XC_6H_6$

	ΔH°_{298}/kJ mol^{-1}			ΔS°_{298}/J K^{-1} mol^{-1}			d(C − X)/Å		
X	DFT (B3LYP)	BAC-MP4	AM1	DFT (B3LYP)	BAC-MP4	AM1	DFT (B3LYP)	BAC-MP4	AM1
Br	*a*	*a*	−14.3	*a*	*a*	−96.1	*a*	*a*	1.99
Cl	−43.4[b]	−30.1	−71.0	−77.9[b]	−91.7	−98.4	2.57[b]	1.86	1.79
CH_3	−41.3	−41.9	−68.49	−127.9	−125.6	−137.5	1.55	1.54	1.52
OH	−70.2	−73.7	−142.6	−116.5	−112.5	−124.1	1.45	1.41	1.42
H	−99.4	−88.7	−145.8	−82.5	−78.3	−84.1	1.11	1.09	1.13
F	−150.2	−138.9	−178.1	−100.8	−97.7	−105.1	1.42	1.39	1.39

[a] Not calculated using this method. [b] Results are in better agreement with those derived from BAC-MP4 calculations when using another functional (see text).

of a series of cyclohexadienyl-type radicals XC_6H_6, with the objective of establishing a scale of stability of those radicals as a function of the nature of the substituent X. Calculations were performed for X = F, Cl, Br, H, OH, and CH_3, which represent various classes of substituents. The few experimental data available were used to validate the results of quantum calculations. In addition to the present determination of the cyclohexadienyl radical stability, two other determinations of the stability of cyclohexadienyl-type radicals, i.e., HOC_6H_6 [23] and ClC_6H_6,[13] have been reported in the literature:

$$\Delta H^\circ_{298}(H + C_6H_6 \rightarrow C_6H_7) = -88 \text{ kJ mol}^{-1} \text{ (this work)}$$

$$\Delta H^\circ_{298}(OH + C_6H_6 \rightarrow HOC_6H_6) = -69 \text{ kJ mol}^{-1} \text{ (ref 23)}$$

$$\Delta H^\circ_{298}(Cl + C_6H_6 \rightarrow ClC_6H_6) \approx -35 \text{ kJ mol}^{-1} \text{ (ref 13)}$$

In addition, it has been shown that the BrC_6H_6 radical must be unstable but no quantitative data could be obtained.[24]

Methods. Calculations were performed using DFT, ab initio (BAC-MP4), and semiempirical (AM1) methods. Using various calculation methods made it possible to estimate a reasonable uncertainty range for the calculated thermochemical parameters for reactions 9:

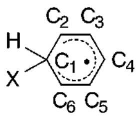
$$X + C_6H_6 \rightleftharpoons XC_6H_6 \tag{9}$$

The density functional theory (DFT) calculations were performed using Becke's three-parameter function [25] and the nonlocal correlation provided by the LYP expression (B3LYP)[26] together with the 6-31G(d) basis set. This method usually gives reliable values for geometries, vibrational frequencies, and energies for stable species. The BAC-MP4 method[27−29] adds bond energy corrections to correlated ab initio Moller−Plesset MP4(SDTQ) energies in order to account for basis set truncation. For open-shell systems, as those we are dealing with here, the method provides an additional correction for spin contamination of the ground state by electronic excited states. DFT and MP4(SDTQ) calculations were performed with the Gaussian 94 program package.[30] The BAC-MP4 corrections were calculated with C. Melius BAC program.[27−29] The AM1 semiempirical method [31] has been applied using the AMPAC program.[32]

In the case of the addition of Br atom to the aromatic ring, only AM1 semiempirical calculations were performed as DFT and BAC-MP4 methods would have cost too much calculation time, given the number of electrons involved.

Results and Discussion. The results of calculations are reported in Table 5 for the series of radicals investigated. They have led to various conclusions which are discussed below.

Optimized Geometry. The optimized structure of XC_6H_6 radicals studied here was found to be the following, whatever the nature of X:



(1) a slight lengthening compared to the C−C bond length in benzene (1.39 Å) was observed for the C_3−C_4 and C_4−C_5 bonds (d = 1.42 Å);

(2) a slight shortening compared to the C−C bond length in benzene (1.39 Å) was observed for the C_2−C_3 and C_6−C_5 bonds (d = 1.37 Å); these bonds thus reflect a stronger C=C double bond character;

(3) a greater distortion was observed for the C_1−C_2 and C_1−C_6 bonds (d = 1.51 Å), these bonds being close to simple C−C bonds;

(4) all C−H bonds are similar (d = 1.07−1.09 Å);

(5) lengths of C−X bonds are similar to those usually observed in molecular species (Table 5) (except for the ClC_6H_6 radical, according to DFT calculations as discussed below);

(6) the cycle remains nearly flat, only a very slight distortion was observed;

It should be noted that DFT/B3LYP calculations lead to an erroneous geometry for the ClC_6H_6 radical, as the calculated C−Cl distance is 2.57 Å, whereas a value of about 1.8 Å is expected for such a bond. It was noticed that structures with shorter C−Cl distances were spin contaminated (not pure ground state), leading to energies higher than expected. Following a recent publication of Braïda et al.,[33] we tried another functional, namely, the BH&HLYP[34] which leads to a better description of two-center/three-electron bonding, as for radicals we are dealing with. Using this functional, the C−Cl distance was found equal to 1.92 Å, i.e., closer to the expected value, and the corresponding spin contamination was also found low. Such complications were not observed for the other radicals, as the

TABLE 6: BDE($X{-}C_6H_6$): Comparison between Experimental and Theoretical Results

X	exptl (kJ mol^{-1})	theor (kJ mol^{-1})
Br	low[a]	< 14[b]
Cl	≈35[c]	30[d]
CH_3	*e*	42
OH	69[f]	70−74
H	88[g]	89−99
F	h	139−150

[a] In agreement with ref 24. [b] Estimated from AM1 calculations. [c] From the equilibrium constant estimated in ref 13 (K_c($Cl + C_6H_6 \rightleftharpoons ClC_6H_6$) = (1−2) × 10^{-18} cm^3 molecule^{-1}). [d] BAC-MP4 result only. [e] Not available but a low value is expected.[37] [f] Reference 23. [g] This work. [h] Not available.

distance of the C−X bond is close to that usually observed in organic molecules.

Entropy. The values of the entropy change for reactions 9, derived from DFT/B3LYP, BAC-MP4, or AM1 calculations, were found to be in satisfying agreement irrespective of the nature of X, except in the case of X = Cl (Table 5). This is consistent with the unexpected optimized geometry derived from DFT/B3LYP calculations, as discussed above. Using the BH&HLYP functional yielded an entropy variation of −91.6 J mol^{-1} K^{-1}, in good agreement with BAC-MP4 and AM1 results.

Reaction Enthalpies and Stability of XC_6H_6 Radicals. The results obtained from $\Delta H°_{298}$ calculation for reactions 9, listed in Table 5, yielded the following order of stability, from the more stable radical to the less one:

$$FC_6H_6 > HC_6H_6 > HOC_6H_6 > CH_3C_6H_6 > ClC_6H_6 > BrC_6H_6$$

Qualitatively, this is in good agreement with experimental data: ClC_6H_6 and BrC_6H_6 could never be observed in laboratory studies[13,24] whereas the equilibrium constant could be measured experimentally for the cyclohexadienyl radical (this work) and for the hydroxycyclohexadienyl radical.[23] In the case of the fluorocyclohexadienyl radical, the ($F + C_6H_6$) reaction path is not clear at the moment, as both abstraction[35] and addition[36] were suggested. For the ($CH_3 + C_6H_6$) reaction, a very low rate constant was measured in the range 372−484 K,[37] indicating that the addition channel is inefficient and, thus, that the $CH_3C_6H_6$ radical is unstable. This is consistent with the results of calculations which show that the stability of $CH_3C_6H_6$ is close to that of ClC_6H_6. As already shown for the latter,[13] the $CH_3C_6H_6$ radical has no chance to be observed in the laboratory, according to our calculations.

Quantitatively, the comparison between experimental and theoretical data concerning the bond dissociation energies, BDE($X{-}C_6H_6$), is given in Table 6. The calculated enthalpy of reaction is in fairly good agreement with the experimental value for the C_6H_7 radical (this work) and for the HOC_6H_6 radical.[23] In the case of the ClC_6H_6 radical, only the BAC-MP4 value is considered for the reasons explained above, but it should be noted that the enthalpy value derived from the DFT/BH&HLYP calculations **($\Delta H°_{298} = -20.1$ kJ mol^{-1})** confirms the results derived from BAC-MP4 calculations, which indicates that the ClC_6H_6 radical is highly unstable. In the case of the BrC_6H_6 radical, the theoretical value derived from AM1 calculations ($\Delta H°_{298} \approx -14$ kJ mol^{-1}) must be an upper limit, since the AM1 values are systematically greater than those obtained by DFT or BAC-MP4 calculations, as shown in Table 5.

The principal conclusion of those results is that none of the Cl, Br, and CH_3 species can add efficiently to the benzene aromatic ring, as a result of the too high instability of the ClC_6H_6, BrC_6H_6, and $CH_3C_6H_6$ radicals.[13,24,37] This is consistent with experimental observations concerning ClC_6H_6 and BrC_6H_6 radicals.[13,24] Considering the fairly good agreement observed between experimental and theoretical results when both data are available, it is suggested that the calculated results obtained for the other radicals (FC_6H_6, $CH_3C_6H_6$) are reliable, with an uncertainty smaller than 10 kJ mol^{-1}. Thus, it is also shown in this work that such calculations can be extended to other cyclohexadienyl-type radicals in order to anticipate their relative stability (qualitative aspect) but also to yield fairly reliable values of their thermochemical parameters.

From the relative stability obtained in the series of radicals investigated, it seems that electronic effects do not play any part in the stability of those radicals. Indeed, the optimized geometry for the XC_6H_6 radicals studied here is similar whatever the substituent X, this suggesting that there is little interaction between X and the π-electron system. As a result, the resonance stabilization energy (RSE) should be nearly the same for all those radicals, as the π electrons are delocalized identically over five carbon atoms of the ring. This has already been suggested for a series of hydroxycyclohexadienyl-type radicals,[38] the proposed RSE value being 69 ± 21 kJ mol^{-1}. The authors pointed out that a greater value is admitted for the cyclohexadienyl radical C_6H_7 (≈100 kJ mol^{-1} [9]), but no explanation for this higher value can be proposed at the moment.

Conclusion

The results reported here provide new experimental data concerning the C_6H_7 radical, to be compared with those of other cyclohexadienyl-type radicals. It is shown that they exhibit similar UV spectra, with an intense peak of absorption around 300 nm, and this is the first time absolute cross sections are determined for the C_6H_7 radical. In addition, it was shown that the C_6H_7 radical is more stable than the HOC_6H_6 radical, which is in good agreement with theoretical calculations performed in this work. A new experimental determination of the enthalpy of reaction 1 is reported, in good agreement both with a previous determination derived from experimental data[12] and with theoretical results.

Experimental data on the C_6H_7 radical were complemented by a more general theoretical study on the stability of a series of XC_6H_6 radicals. The scale of stability derived from theoretical calculations is qualitatively consistent with experimental observations, and, in addition, the calculated values of thermochemical parameters are in fairly good agreement with the few experimental data available. As a result, it is shown in this work that such calculations can be extended to other cyclohexadienyl-type radicals in order to calculate their thermochemical parameters with a good degree of confidence.

Theoretical calculations also showed that Cl and Br atoms cannot add to the aromatic ring because the corresponding adduct is very unstable. This is consistent with the fact that at room temperature, the reactions (Cl + toluene) and (Cl + phenol) proceed 100% via abstraction of an H atom from the substituent (leading respectively to benzyl and phenoxy radicals), and also with the fact that Cl atoms do not react with chlorobenzene, as reported by Sokolov et al.[13]

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Note Added in Proof. The C_6H_7 spectrum was also reported by E. Bjergbakke, A. Sillesen and P. Pagsberg, (*J. Phys. Chem.*, **1996**, *100*, 5729); the shape is in fairly good agreement with the shape of our spectrum but the absorption cross section is a factor five smaller.

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